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(54) Title: BIAXIALLY ORIENTED COPOLYESTER FILM FOR CAPACITOR DIELECTRIC USE OR THERMAL TRANSFER RIBBON USE

(57) Abstract

The present invention comprises a biaxially oriented copolyester film useful for capacitor dielectrics or thermal transfer printing ribbons. Such films have good winding characteristics, slipperiness, good mechanical properties (stiffness and strength), and excellent thermal stability. The biaxially oriented copolyester film has at least 25 mole percent of the dicarboxylic acid or its ester equivalent content in the copolyester of 4,4'-bibenzoic acid. The remainder of the copolyester is such that the melting point is about 260 °C such that the copolyester is capable of withstanding a thermal treatment of 260 °C for about 10 seconds. The biaxially oriented copolyester film also includes an effective amount of fillers having a bimodal particle distribution sufficient to provide slip and good winding characteristics such as those that are known in the art. The bimodal particle distribution generally should comprise: (a) fine particles having an average particle diameter of 3 to 50 nm and employed in the range of from about 0.01 to about 3 percent by weight based on weight of the copolyester, and (b) a large particle distribution having an average particle diameter of 0.05 to 4 µm and an aspect ratio of from 1.0 to 1.2 and being employed in the range of 0.005 to 1 percent by weight based on the weight of the copolyester.

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## BIAXIALLY ORIENTED COPOLYESTER FILM FOR CAPACITOR DIELECTRIC USE OR THERMAL TRANSFER RIBBON USE

### Background Of The Invention

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#### (1) Field Of The Invention

This invention relates to a biaxially oriented PENBB copolyester film having low shrinkage properties and good thermal properties for use as a capacitor dielectric film or as a thermal transfer film. In particular, the film of the present 10 invention must have good winding characteristics as well as slipperiness to permit the film to slide over a previously wound section (i.e., to be non-blocking). In addition to the above characteristics, the film of the present invention has good stiffness (tensile modulus) and mechanical strength and thus thickness reduction can be achieved to make the film of the present invention exceptionally 15 useful as a capacitor dielectric or as a thermal transfer ribbon material.

#### (2) Prior Art

Many prior art patents profess to disclose a satisfactory polymeric film capable of being employed as a material for capacitors and for thermal transfer 20 ribbons. However, there are no commercially available films which have the outstanding properties of the present invention. Chiefly lacking in the prior art films is thermal stability. Thermal stability is important because a capacitor incorporating the dielectric film must be run through a solder bath at approximately 260°C during surface mounting assembly to solder the leads of the 25 capacitor to a circuit board. The majority of the prior art films fail due to melting and/or shrinking during or shortly after exposure to a solder bath. Because the yield in such a process is particularly low, the cost of the circuits using these film capacitors is prohibitively high. Therefore, up until now ceramic capacitors had to be used for surface mounted circuits at the price of dielectric properties

inferior to those of film capacitors. There is a need for the improved dielectric properties of a film capacitor in capacitors suitable for surface mounting.

A high melting point and low thermal shrinkage values are also desirable in thermal transfer ribbons, in order to allow high printing head temperatures without causing the sticking or distortion of the printing ribbon.

Another desired characteristics of capacitor dielectric films is a low water pickup. Low water pickup is important because this retards the degradation of the capacitor due to corrosion of the metallized layer. With the present invention, a film water pickup at 23 °C and 50 % r.h. of less than 0.1 weight percent and preferably less than 0.06 weight percent are possible.

European Patent Application No. 423,402 filed October 17, 1989 by Teijin Limited, discloses a thermoplastic polymeric film said to have usefulness as a material for capacitors and for thermal transfer ribbons. This patent discloses that the polymeric substrate can be polyester, polyphenylene sulfides, polyamides, polysulfones, and polyvinylidene fluoride. While some of these polymers have good thermal characteristics, they are either very expensive to produce or have poor mechanical properties that limit their usefulness for capacitor films or thermal transfer ribbons.

In an attempt to make polymers more thermally stable and particularly polyester polymers, copolymers of polyethylene naphthalate/4,4'-bibenzoate are described below.

U.S. Patent No. 3,008,934 discloses copolymers containing as acid derived units 4,4'-bibenzoate and a host of other dicarboxylates including 2,6-naphthalic dicarboxylate. It also discloses oriented fibers and films prepared from these copolymers, however, biaxially oriented PENBB films are not disclosed or envisioned. In particular, those films with improved stiffness (tensile modulus) and tensile strength in both MD and TD as well as thermostability, UV stability, hydrophobicity, dimensional stability and impermeability toward gases in comparison to PET film are not disclosed in U.S. Patent No. 3,008,934.

30 Japanese Patent No. 50/135333 to Teijin Limited describes a fiber material

composed of a copolyester of polyethylene naphthalate with 0.5 to 20 mole-% 4,4'-bibenzoate units. In accordance with the teachings of this patent, a 4,4'-bibenzoate content higher than 20 mole-% is disadvantageous because the melting point (about 237 °C) of the resulting polymer is significantly below that of polyethylene terephthalate (PET) (meaning that the thermal stability is also lower). Specifically, this patent teaches that a very small mole percent of 4,4'-bibenzoate (0.5 to 3 mole-%) results in a melting point higher than PET and thus yields better thermal stability during processing. Therefore, as the percentage of 4,4'-dimethyl bibenzoate increases, the melt point, and thus thermal stability, 10 decreases according to this reference.

There continues to be a need for a thermoplastic polymer having excellent thermal stability characteristics and having the requisite stiffness (tensile modulus) and mechanical strengths sufficient to permit those skilled in the art to produce a film capable of being employed as a capacitor film or as a thermal 15 transfer film.

### Summary Of The Invention

The present invention relates to a biaxially oriented PENBB copolyester film having at least about 25 mole-% of the diacid or derived content in the 20 copolymer of 4,4'-bibenzoic acid or of 4,4'-dialkyl bibenzoate with the remainder of the copolyester being produced from a different diacid or diester. The copolyester must have a melting point sufficient to permit the copolymer to withstand a solder bath such as those known in the capacitor dielectric manufacturing industry, i.e., the biaxially oriented copolyester film must not melt 25 or shrink to a significant extent. With the present invention, shrinkages of less than 0.5 percent at 150 °C are possible, preferably films having a shrinkage of less than 0.3 percent are possible.

Furthermore, a biaxially oriented PENBB copolyester film useful for capacitor dielectrics or thermal transfer printing ribbons must also have good 30 winding characteristics, slipperiness, as well as the stiffness and mechanical

strength to form an ultrathin film. The reason thickness reduction of polymeric films employed for dielectric material in a capacitor is advantageous because the electrostatic capacitance of the capacitor is proportional to the dielectric constant of the dielectric material and inversely proportional to the square of the thickness of the film. If the dielectric material is constant, reducing the thickness of the film provides a very significant improvement in size reduction and capacitance increase for the manufactured capacitors.

In thermal transfer ribbon printing, the film must also be thin so that the printing head can be activated with a low energy in order to meet the needs of high speed printing. Moreover, a thickness reduction of the polymer film produces crisper letters and figures by permitting improved heat flow from the printing head to the transferred printing layer.

In addition to thickness, it is necessary for films used in capacitors and for thermal transfer ribbons to have good handling characteristics. Thermoplastic films generally do not slide with respect to themselves. In fact, such films usually produce blocking in which layers of the film refuse to slide over one another unless an unnecessarily high force is employed. Such a force often scratches or destroys the flatness of the film and sometimes even causes breakage. In order to provide sufficient slip and good winding characteristics of a film, it is known to employ fine protrusions or depressions on the surface of the film. Such protrusions or depressions on the surface of the film are made by incorporating into the thermoplastic polymer fine inert "filler" particles. Such characteristics may be achieved with a bimodal particle distribution. Such filler particles are generally disclosed in the above identified European Patent Application No. 423,402.

With the present invention, a bimodal particle distribution of filler material is employed to provide sufficient slip and good winding characteristics. These particles may also be in the form of agglomerated fine particles which, upon blending with the polymer resin and subsequent film processing, break up into finely divided particles.

In the broadest sense, the present invention comprises a biaxially oriented copolyester film useful for capacitor dielectric or thermal transfer printing ribbons, wherein the biaxially oriented copolyester film has at least 25 mole-% of the diacid derived content of the copolyester of 4,4'-bibenzoate units, and having a 5 melt point sufficient to withstand a thermal treatment of at least about 260°C or higher for about 10 seconds; and incorporating into the copolyester an effective amount of one or more fillers having a bimodal particle distribution sufficient to provide slip and good winding characteristics.

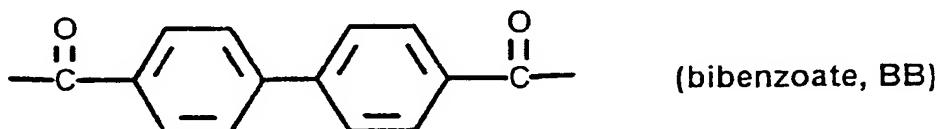
#### 10 Brief Description Of The Drawing

Figure 1 is a graph showing the dependence of the melting point temperature of the preferred PENBB copolyester, polyethylene 2,6-naphthalate/4,4'-bibenzoate, on its molar diacid ratio.

#### 15 Description Of The Preferred Embodiments

Generally the PENBB copolymers of the present invention are made by reacting at least two dicarboxylic acids, or their ester equivalents with suitable glycols or diols, as is well known in the art. Such a reaction produces monomers or oligomers of the copolyester. The monomers or oligomers are then subject to 20 a polycondensation reaction, as known in the art, to produce a copolyester.

The PENBB copolyester of the present invention is derived primarily from dicarboxylic acids or their ester equivalents with at least 25 mole percent of the dicarboxylic acid being 4,4'-bibenzoic acid (or the ester equivalent) having the following formula:



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The remainder of the copolyester may be formed from other dicarboxylic acids or their ester equivalents, such as terephthalic acid, isophthalic acid,

phthalic acid, naphthalene-2,6-dicarboxylic acid, 1,4 cyclohexane dicarboxylic acid, di-(4-phenyl)-acetylene dicarboxylic acid; 1,2 di-(4-phenyl)-ethylene dicarboxylic acids, sebacic acid, malonic acid, adipic acid, azelaic acid, glutaric acid, suberic acid, succinic acid, and the like, or mixtures of these can be 5 employed in the present invention. Naphthalene-2,6-dicarboxylic acid is the preferred remainder diacid.

Suitable diols employed in the present invention include ethylene glycol, diethylene glycol, polypropylene glycol, butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,10-decanediol, cyclohexane dimethanol, and the 10 like. Ethylene glycol is the preferred glycol.

Suitable copolymers of the present invention can comprise, for example, polyethylene terephthalate/4,4'-bibenzoate, polybutylene terephthalate/4,4'-bibenzoate, polypropylene terephthalate/4,4'-bibenzoate, polyethylene naphthalate/4,4'-bibenzoate, polyethyleneterephthalate/isophthalate/4,4'-bibenzoate, 15 polyethylene terephthalate/adipate/4,4'-bibenzoate, polyethylene terephthalate/-sulphoisophthalate/4,4'-bibenzoate, and the like.

In order to achieve the desired mechanical properties in the biaxially oriented PENBB film it is recommended that the IV value (inherent viscosity, as measured in a 1 : 1 weight-ratio mixture of pentafluorophenol and hexafluoroisopropanol at a concentration of 0.2 g/dl and a temperature of 25 °C) of the 20 PENBB polymer after extrusion be > 0.5 dl/g and preferably > 0.55 dl/g.

In a preferred embodiment, a polyethylene naphthalate bibenzoate copolyester is made from equimolar portions of the esters 2,6-dimethyl naphthalate and 4,4'-dimethyl bibenzoate, or the acids of naphthalene-2,6-dicarboxylic acid and 4,4'-bibenzoic acid. The copolyester is obtained by 25 polycondensation of the diacids or diesters with a diol. It may be advantageous, however, to employ an excessive amount of the diol in order to influence the reaction kinetics. After the reaction of the diacids or diesters with the diol, a polycondensation reaction is carried out according to known processes. For the 30 preferred embodiment, a mixture of two or more dicarboxylic acids/esters are

mixed with at least 100 mole percent of the corresponding diol. The diacids or their ester equivalents and the diols are mixed uniformly and heated to approximately 200°C in the presence of a transesterification catalyst, as is well known in the art. The reaction yields oligomeric or low molecular weight 5 polyester which is subsequently subjected to the polycondensation reaction in the presence of polycondensation catalyst. Additionally, stabilizers, antioxidants, delustrants, pigments, fillers, antistatic agents, etc., may be uniformly mixed with the copolyester.

Suitable catalysts are antimony, manganese, cobalt, magnesium, zinc, 10 calcium, etc., as are well known in the art. The preferred transesterification catalyst, where employed, would be manganese and/or cobalt. The preferred polycondensation catalyst would be antimony compounds. Such catalysts are well known and conventional in the prior art.

The polyester film of the present invention can be manufactured by an 15 extrusion process. The polyester resin is first heated to a molten state and then extruded through a wide slot die in the form of an amorphous sheet onto a polished, revolving casting drum. The amorphous sheet is rapidly cooled or "quenched" to form a cast sheet of polyester. The cast polyester sheet is removed from the casting drum and then axially stretched in one direction, either 20 in the direction of the film travel (machine direction) or perpendicular to the machine direction (transverse direction), while being heated to a temperature between the glass transition temperature and about 30°C above the cold crystallization temperature (both temperatures can easily be measured on the films by differential scanning colorimeter (DSC)).

25 The copolyester film is biaxially oriented (stretched in both the machine direction and the transverse direction). The total stretch ratios in the machine direction and the transverse direction lie between 1:2 and 1:10, preferably between 1:2.5 and 1:5. The product of the total stretch ratios should be between 1 to 30, and preferably between 5 to 20. Biaxial drawing is performed 30 such that the birefringence is < 0.2, preferably < 0.1 to ensure adequately

isotropic properties. Birefringence as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

5 After biaxial orientation of the film, a heat setting step takes place to lock in the properties of the film. The heat setting occurs at a temperature between the cold-crystallization temperature and the melt temperature of the copolymer composition. After heat setting, the film may be wound on a roll, or in some cases surface treatment of the film such as corona treatment, plasma or flame 10 treatment may be employed before winding the film on the roll, particularly where the film will be further coated with a primer coating or a metallic coating, for example.

It is desirable for the film to have a final total thickness of between 0.1 and 12  $\mu\text{m}$ , preferably between 0.3 and 6  $\mu\text{m}$ .

15 No matter what copolyester composition is employed, the capacitor incorporating the film thereof must be able to withstand a solder bath which is typically in the range of about 260 °C for about 10 seconds. Copolymers which can survive this conditioning are thermally stable for the present invention. Copolymers of the present invention typically have a melting point dependent 20 upon the composition. Figure 1 illustrates a melting point curve based on a preferred composition of PENBB. Similar curves are also expected for other copolymers of the present invention.

25 In order to provide good handling and winding properties, the film composition must be such that the surface is rough. This is achieved by incorporating fine inert insoluble particles ("filler") into the film. The fine inert insoluble particles can be in the form of an agglomerate which disperses or breaks up upon orientation of the film to form fine inert insoluble particles. Generally, these fine particles may be added, preferably to the monomers before 30 or during polycondensation or to the polymer before extrusion. Such inert fine particles either in agglomerated form or finely dispersed powders can be kaolin,

talc, silica, carbonates of magnesium, calcium, or barium; sulfates of calcium, or barium; phosphates of lithium, calcium, or magnesium; oxides of aluminum, silicon, titanium, zirconium, or mixtures thereof, lithium fluoride, carbon black, or the organic acid salts of calcium, barium, zinc, and manganese. It is also 5 possible to use fine particles made of crosslinked polymers such as polystyrene, polyacrylate, or polymethacrylate, for example, which are inert with respect to the reactions described herein to make the copolyester.

The particles may be of one type or mixtures of several types. The shapes 10 of the particles can be irregular, flaky, spherical, or elongated. Preferably, spherical particles are employed particularly for the large particles. The hardness, density and color of the particles is generally immaterial. The average size of the particle should be less than 10  $\mu\text{m}$ , and generally preferably less than 3  $\mu\text{m}$  as will be discussed later. The amount of filler incorporated into the film should generally be in a range of from 0.01 % to 4 % by weight and preferably between 15 0.5 % and 2.0 % by weight, based on the weight of the polyester.

For the present invention, it is preferable to have a bimodal particle distribution, i.e. particles of a large size distribution and particles of a small size distribution.

The bimodal particle distribution for the present invention comprises from 20 about 0.01 to about 3 % by weight of inert particles based on the weight of the copolyester, and has an average particle diameter of 2 to 50 nm which optionally may be aggregates of the fine particles, said aggregates having an average particle diameter of 0.05 to 5  $\mu\text{m}$ . The other modal particle distribution consists of 0.005 to 1 % by weight, based on the weight of the copolyester, and has an 25 average particle diameter of 0.05 to 4  $\mu\text{m}$  and are preferably nearly spherical with an aspect ratio of from 1.0 to 1.2. (The aspect ratio of a particle is the ratio of the length of its longest axis to its shortest.)

The content of the fine inert particles should be in a range from 0.01 to 30 3 % by weight based on the weight of the copolyester. If the content is less than 0.01 % by weight, the excess air is trapped between the layers upon

winding. On the other hand, if the fine particle mixture exceeds 3 % by weight, the film's surface is excessively roughened and the dielectric breakdown voltage of the film is decreased. The larger particles are more spherical in shape and differ from the ultra fine lumpy particles. The larger particles have a particle size 5 of about 0.5  $\mu\text{m}$  and are present in a range of 0.005 to 1% by weight, based on the weight of the copolyester. Preferably, the average particle diameter of the large particles is not larger than the thickness of the film. Preferably, the large particle diameters size is between about 0.2 and 3  $\mu\text{m}$ . If the large particle size 10 is less than 0.05  $\mu\text{m}$ , the resulting film has insufficient slipperiness and suffers from processability. If it exceeds 4  $\mu\text{m}$  in size, the surface of the film is excessively rough and the dielectric breakdown voltage is decreased and insulation defects increase.

The bimodal particle distribution described in the present invention is generally similar to that described in European Patent Application No. 423,402, 15 as previously described. With the present invention, however, it is contemplated that a broader range (types) of inert particles can be employed for both the fine particle size and the large particle size.

#### EXAMPLE 1

20        289 parts by weight of dimethyl 2,6-naphthalene dicarboxylate, 322 parts by weight of dimethyl 4,4'-bibenzoate, 368 parts by weight of ethylene glycol and 0.7 parts of manganese acetate tetrahydrate are initially introduced into a conventional polycondensation reactor provided with a blanketing gas line ( $\text{N}_2$ ), pressure equalization, a thermometer, a condenser, a vacuum connection and a 25 stirrer. The mixture is heated at 220 °C for 2.5 hours, during which time methanol is distilled off. 0.675 parts by weight of triphenyl phosphate and 0.23 parts of antimony trioxide are then added as polycondensation catalysts and the mixture is heated to 270 °C, with stirring. Vacuum is applied and the temperature is raised to 285 °C and maintained for 2.5 hours. The melt is then pelletized. 30        The pellets are white, opaque and crystalline. An IV value of 0.56 dl/g is

determined for the pellets (measured at a concentration of 0.1 g/ml in pentafluorophenol/hexafluoroisopropanol [weight ratio 1:1] at 25 °C). The pellets are further reacted for 20 hours at 240 °C under vacuum in the solid phase. After this treatment the IV value is 1.1 dl/g. As expected, no  $T_g$  or  $T_{cc}$  is discernable 5 in the DSC recording for the crystalline granules condensed in the solid phase; the melting point ( $T_m$ ) is 281 °C.

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## EXAMPLE 2

The polymer of Example 1 is heated to a molten state (about 305 °C) in a twin screw mixing extruder (1000 g) and 6 g of a fine porous silica powder (0.6 percent by weight of the polymer) having an aspect ratio of 10 and an average particle diameter of 3 - 50 nm, is added to the molten polyester. 15 Additionally, 3 g of a generally spherical silica powder (0.3 % by weight, based on the weight of the polymer) having an aspect ratio of 1.1 and an average particle diameter of 0.05 to 4  $\mu\text{m}$  is added to the molten polymer. After uniform mixing, the polymer is pelletized. The pellets are then dried and fed into a single screw extruder and extruded on to a chilled casting drum and then biaxially 20 oriented at 130 °C by stretching 3.9 times in the MD and stretching 4.0 times in the TD. The film is heatset at 260 °C for 10 seconds. The film has a final thickness of 3.5  $\mu\text{m}$ .

The film produced in accordance with Example 2 has a surface roughness of about 110 nm; a shrinkage measured at 150 °C in a forced air oven of about 25 0.3 percent in both the MD and TD; a slip of about 0.37/0.35 (static friction/organic friction) according to ASTM D-1894B-63; moisture absorption at 50 percent relative humidity at 23 °C of 0.04 percent.

Thus, it is apparent that there has been provided, in accordance with the invention, a biaxially oriented PENBB copolyester film useful as a capacitor 30 dielectric film or as a thermal transfer ribbon film, that fully satisfies the objects,

aims, and aspects set forth above. While the invention has been described in conjunction with the specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace 5 all such alternatives, modifications, and variations as fall within the sphere and broad scope of the present invention.

## THAT WHICH IS CLAIMED IS:

1. A biaxially oriented copolyester film comprising:
  - (a) a biaxially oriented PENBB film and
  - (b) an effective amount of one or more fillers uniformly blended within said PENBB and having a bimodal particle distribution sufficient to provide slip and good winding characteristics.
2. The biaxially oriented copolyester film of Claim 1 in which the PENBB is a copolyester having at least 25 mole-% of the dicarboxylic acid derived repeat units consisting of 4,4'-bibenzoate units and having a melting point at least sufficient to withstand a thermal treatment of about 260°C for about 10 seconds;
3. The biaxially oriented copolyester film of Claim 1 or 2 in which the PENBB is selected from the class consisting of polyethylene terephthalate/4,4'-bibenzoate, polybutylene terephthalate/4,4'-bibenzoate, polypropylene terephthalate/4,4'-bibenzoate, polyethylene naphthalate/4,4'-bibenzoate, polyethylene terephthalate/isophthalate/4,4'-bibenzoate, polyethylene terephthalate/adipate/4,4'-bibenzoate and polyethylene terephthalate/sulphoisophthalate/4,4'-bibenzoate.
4. The biaxially oriented copolyester film of Claim 3, wherein the PENBB is polyethylene naphthalate/bibenzoate.
5. The biaxially oriented copolyester film of Claim 4, wherein the acid derived portion of the PENBB consists of 40 to 60 mole-% of naphthalene-2,6-dicarboxylate and 60 to 40 mole-% of 4,4'-bibenzoate units.
6. The biaxially oriented copolyester film of any of the Claims 1 to 5, wherein

said bimodal particle distribution comprises:

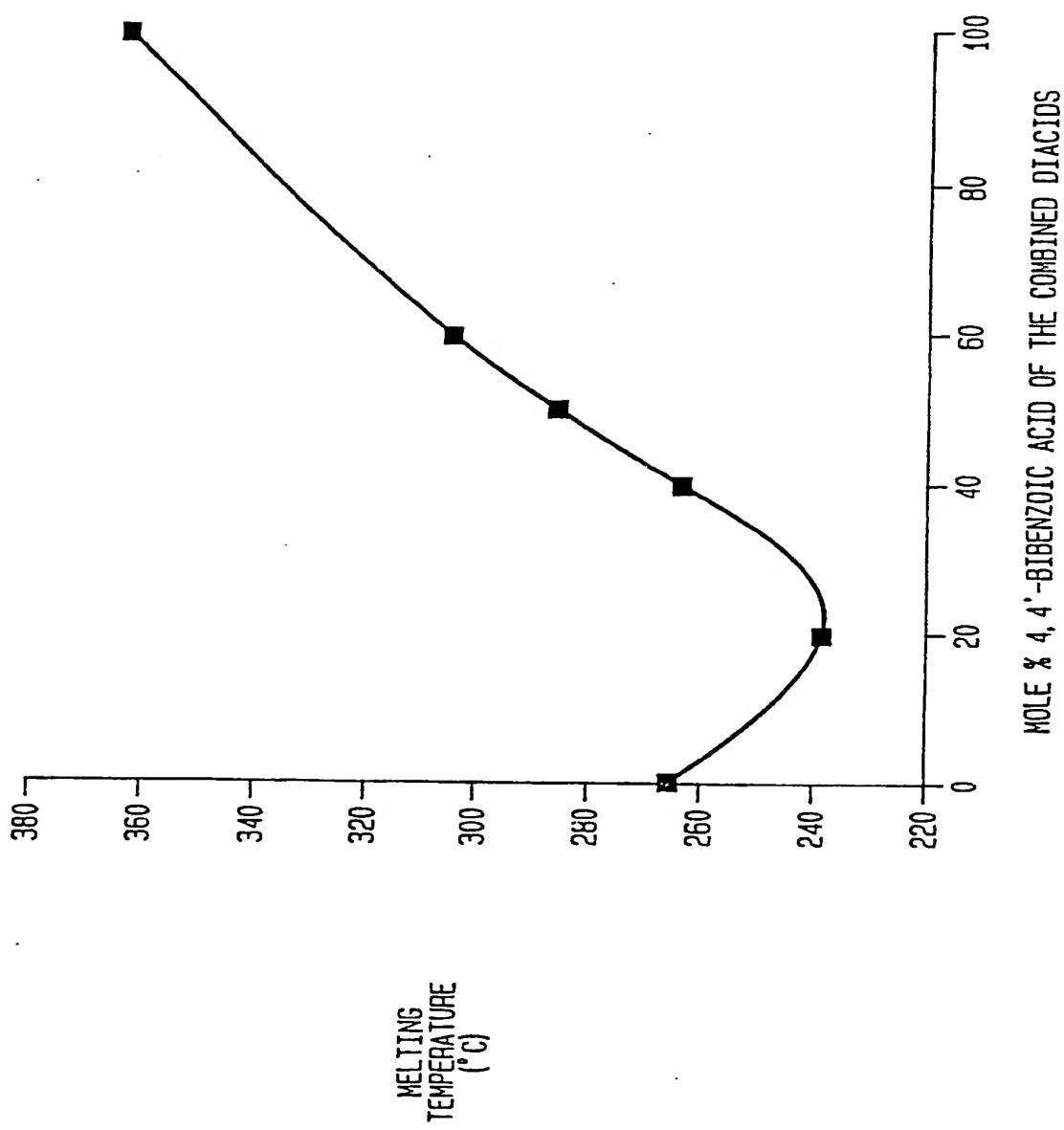
- (a) fine particles of 0.01 to 3 % by weight and having an average particle diameter of 3 to 50 nm, and
- 5 (b) 0.005 to 1 % by weight of large generally spherical or nearly spherical inert particles having an average particle diameter of about 0.05 to 4  $\mu\text{m}$  and an aspect ratio of from 1.0 to 1.2, all amounts based on the weight of said copolyester.

7. The biaxially oriented copolyester film of any of the Claims 1 to 6, wherein  
10 said bimodal particle distribution comprises particles which are selected from the class consisting of kaolin, talc, silica, carbonates of magnesium, calcium, or barium; sulfates of calcium or barium; phosphates of lithium, calcium or magnesium; oxides of aluminum, silicon, titanium, zirconium, and mixtures thereof; lithium fluoride, carbon black, and the organic acid salts of calcium,  
15 barium, zinc, and manganese; and crosslinked polymers.

8. The biaxially oriented copolyester film of any of the Claims 1 to 7, wherein the birefringence of the film is < 0.2 and wherein the IV-value of the PENBB is > 0.5 dl/g.

- 1 / 1 -

FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/10710

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : E32B 3/10, 5/16, 27/06  
 US CL : 428/323, 327, 328, 329, 330, 331, 480, 910, 141

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/323, 327, 328, 329, 330, 331, 480, 910, 141

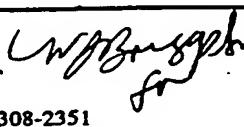
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,793,132 (BHAKUNI ET AL) 19 FEBRUARY 1974. Entire document.	1-5
A	US, A, 3,991,013 (PLETCHER) 09 NOVEMBER 1976 Entire document.	1-5
A	US, A, 4,781,963 (UTSUMI ET AL) 01 NOVEMBER 1988. Entire document.	1-5
A	US, A, 3,714,772 (BHAKUNI ET AL) 06 FEBRUARY 1973. Entire document.	1-5
A	US, A, 5,069,942 (ANDERSON) 03 DECEMBER 1991. Entire document.	1-5

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*A*	Special categories of cited documents: document defining the general state of the art which is not considered to be part of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E*	earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L*	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O*	document referring to an oral disclosure, use, exhibition or other means	*&*	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 MARCH 1993	16 APR 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer ROBERT FOLLETT 
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)\*

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US92/10710

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 6, 7, 8  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.